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Properties of Styrene-Methyl Methacrylate Copolymers with Different Architectures: Thermodynamic and Conformational Properties in Dilute Solution

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Methods for characterization and preparation of copolymers with different architectures are briefly described. The dilute solution properties of alternate, random, and block copolymers of styrene and methyl methacrylate are discussed placing emphasis on examining their dependences on the molecular architectures, particularly, on the modes of monomer arrangement. The unperturbed dimensions of the block copolymers are more nearly equal to the averages of the parent homopolymers, whereas those of the random copolymers are slightly larger than the averages, implying the presence of extra short range interactions. From the analyses of the composition dependence of the θ temperatures and the intrachain excluded volume parameters for solutions of the random and the block copolymers, it has been found that the extra (repulsive) interactions between the chemically different species are playing an important role in the random copolymer solutions. However, in the block copolymer solutions the presence of such interactions is not observed, as opposed to previously reported observations.

INTRODUCTION

The properties of copolymers are more complex than those of homopolymers because of the complexity and versatility in the architecture of copolymer molecules. To characterize a copolymer sample consisting of a given set of structural elements (monomers), it is necessary to specify at least three factors: The total number of elements linked together to form a polymer chain (the molecular weight), the fraction of each element in a chain (the composition), and the mode of monomer arrangement (the sequence length distribution). Occasionally the knowledge of stereochemical configuration along the skeletal chain would be required also.

Any copolymer sample is usually an assembly of more or less different molecules: The properties of each species are obviously dependent on these three factors, the molecular weight, the composition, and the sequence length distribution. It is of interest, therefore, to find out how the properties of copolymers may be related to the molecular architecture. What one usually observes as the property of a whole copolymer sample is the average of the values over all the species

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involved: Moreover, the averaging process is different depending on the type of particular properties one is concerned with. Hence the heterogeneities on these factors should be important to interpret the properties of a copolymer system.

In this review we will discuss some problems in the studies on copolymer solutions. First we briefly discuss the methods for characterization of copolymer sample based on the use of dilute solution properties, and the relation between monomer reactivities and molecular architectures. We also describe some of our recent studies on the effect of monomeric arrangements on the conformational and thermodynamic properties of styrene-methyl methacrylate copolymers with different architectures. The behavior would be generally valid for any amorphous (noncrystallizable), linear, binary copolymer which consists of any incompatible homopolymer pair.

CHARACTERIZATION OF COPOLYMER SAMPLES

Average Composition and Average Molecular Weights: We consider a linear copolymer consisting of two monomer species, A and B. The average composition of the whole sample, expressed either by mole fraction m or by weight fraction x (with respect to species A), may be easily determined depending on the nature of copolymers to be studied, by elementary analysis, by spectroscopic methods, and so on. There are no fundamental difficulties in exercising these procedures.

On the contrary, it is rather difficult to estimate the composition heterogeneity[1,2]. A possible measure is the fractionation method[3] with an appropriate choice of solvent-nonsolvent systems: For example, it is reported that styrene (ST)-methyl methacrylate (MMA) copolymers may be fractionated with respect to composition by using toluene-acetonitrile system, while they may be fractionated with respect to molecular weight by butanone-diisopropyl ether system.

A partial analysis is possible, as will be discussed below, by light scattering method[2] and by ultracentrifugation methods (*e.g.*, Archibald method, sedimentation equilibrium). A more complete analysis may be possible by the density gradient sedimentation method[4], although the procedure appears to be rather complicated. Very recently the application of thin layer chromatography has been proposed for the analysis of composition heterogeneity[5]. The method appears to be quite promising.

Number average molecular weight M_n of a copolymer sample may be determined by use of colligative properties: The cryoscopy, the ebulliometry, and the osmometry are applicable to copolymer solutions without fundamental difficulties. The average composition x (by weight fraction of component A) may be related to M_n as:

$$x = M_n^{\mathrm{A}}/M_n\,;\; M_n = M_n^{\mathrm{A}} + M_n^{\mathrm{B}} \tag{1}$$

where M_n^{A} and M_n^{B} are the number average molecular weights with respect to component A and B, respectively[2].

On the contrary, conventional methods such as light scattering (LS)[1,2] and sedimentation equilibrium would not provide a weight average molecular weight M_w but an apparent value, if they are applied to a copolymer system with composition heterogeneity. Stockmayer *et al.*[1] and Benoit *et al.*[2] have shown that the

light scattering molecular weight M_{app} of a heterogeneous copolymer is expressed as:

$$M_{app} = M_w + 2bP + b^2Q \tag{2}$$

$$P = \sum \gamma_i M_i (x_i - x);\ Q = \sum \gamma_i M_i (x_i - x)^2 \tag{2a, b}$$

$$b = (\nu_1 - \nu_2)/\nu \tag{3}$$

where the parameters P and Q represent the heterogeneity in composition such as defined by Eqs. (2a, b): P relates to the composition variation with molecular weight (first moment), and Q to its broadness (second moment); γ_i is the weight fraction of component i which has molecular weight M_i and composition x_i; ν_1, ν_2, and ν are the specific refractive index increments of the parent homopolymers A and B, and the copolymer, respectively. Therefore, LS measurements in several solvents with different b-values allow one to determine M_w, P, and Q of a given copolymer sample. Values of ν_1 and ν_2 vary with the refractive index of solvent, but value of $(\nu_1 - \nu_2)$ is almost independent of solvent and is nearly a constant for a given comonomer pair. Therefore the above procedure, as a measure for the heterogeneity analysis, is not applicable to copolymers consisting of a homopolymer pair for which $\nu_1 = \nu_2$ in a solvent. An information similar to the LS method is obtained also by the Archibald ultracentrifugation method[6]. The Archibald apparent molecular weight $\overline{M}_{app}$ may be given as:

$$\overline{M}_{app} = M_w + (a+b)P + abQ \tag{4}$$

$$a = (\beta_1 - \beta_2)/\beta \tag{5}$$

where β_1, β_2, and β are the buoyancy factor $(1 - \bar{v}\rho_0)$ ($\bar{v}$ is the partial specific volume of polymer; ρ_0 is the solvent density) of the parent homopolymers and the copolymer, respectively. The equation (4) involves two variables dependent on the solvent nature, hence, is less convenient than the LS Eq. (2). Nevertheless, the Archibald method may be complementary to the LS method, for it is advantageous for the analysis of low molecular weight materials. Table 1 shows a few examples of the LS and the Archibald analysis. Agreement between the two methods is reasonably good[6].

Benoit[2] has shown that the weight average molecular weight M_w may be related to the values of constituent components as:

$$M_w = xM_w^A + (1-x)M_w^B + 2M_w^{AB} \tag{6}$$

$$M_w^{AB} = \sum \gamma_i x_i (1 - x_i) M_i \tag{6a}$$

Here M_w^{AB} is a cross (heterogeneity) coefficient, which takes the following values in two extreme cases: $M_w^{AB} = 0$ for a homopolymer blend; and $M_w^{AB} = x(1-x)\ M_w$ for a copolymer homogeneous in composition ($x_i \equiv x$). In general, a simple additivity rule does not hold for M_w, as opposed to M_n, of a copolymer sample[2].

As a measure for molecular weight distributions, it is customary to take the value of M_w/M_n. Likewise, the heterogeneity in composition may be expressed by the parameters P and Q. These quantities are closely related[2]; *i. e.*,

$$M_w/M_n = x^2(M_w^A/M_n^A) + (1-x)^2(M_w^B/M_n^B) + 2M_w^{AB}/M_n \tag{7a}$$

$$P = x(1-x)(M_w^A - M_w^B) + (1-2x)M_w^{AB} \tag{7b}$$

$$Q = x(1-x)[(1-x)M_w^A + xM_w^B - 2M_w^{AB}] \tag{7c}$$

Table 1. Summary of Characterization Data on Some ST-MMA Copolymer Samples.

Code	ST-wt%	$10^{-4}M_n$	$10^{-4}M_w$[a]	P/M_w	Q/M_w	$10^{-4}M_n{}^A$	Precursor. PST $10^{-4}M_n$	$10^{-4}M_w$
Random Copolymers								
SM5-10	54.0	18.5	(LS) 18.5	0	0	—		
SM5-5	55.0	39.7	(LS) 60.8	0	0.08	—		
			(A) 70.3	0	0.08			
SMA12	50.2		(LS) 11.4	0	0	—		
			(A) 11.4	0	0			
Block Copolymers								
22B	45.2	70.7	(LS) 76.8	−0.015	0.017	32.0	31.6	32.2
25B	50.7	14.9	(LS) 25.9	−0.07	0.11	7.55	6.75	13.5
			(A) 28.4	−0.07	0.11			
26B	46.0	34.6	(LS) 35.0	−0.003	0.004	15.9	14.7	—

[a] (LS)=light scattering; (A)=Archibald method.

Particulary for a block copolymer prepared by random coupling of two homopolymers as in the case of an anionic polymerization method and of the coupling through functional terminal groups, no correlation should exist between the molecular weights of A and B parts in a chain (assuming that the activity of functional terminals does not depend on its chain length), thus one obtains for Eq. (6a):

$$M_w{}^{AB} = M_n{}^A M_n{}^B / M_n = x(1-x)M_n \tag{6b}$$

Combining Eq. (6a) with Eqs. (7a, b, c) one readily obtains;

$$M_w/M_n = 1+x^2Y^A+(1-x)^2Y^B \tag{8a}$$

$$P = x(1-x)[xY^A-(1-x)Y^B]M_n \tag{8b}$$

$$Q = x^2(1-x^2)[Y^A+Y^B]M_n \tag{8c}$$

$$M_w{}^A/M_n{}^A = 1+Y^A;\ M_w{}^B/M_n{}^B = 1+Y^B \tag{8d, e}$$

For block copolymers, the quantities such as Y^A, Y^B, and M_n could be independently evaluated. Then the values of M_w, P, Q may also be evaluated by Eqs. (8a-e) from M_n, Y^A and Y^B data. The results are in reasonable agreement with the directly observed values.

Run Number and Monomer Reactivities: The mode of monomer arrangement may be most conveniently described in terms of *rum number* $\overline{R}$ introduced by Harwood and Ritchey[7]. This is defined as the average number of runs of like monomer or monomers in a copolymer chain per 100 monomer units. Using the run number $\overline{R}$ and the average composition m (by mole fraction of A) of a given copolymer, one can calculate number fractions of any kinds of diads (*e.g.*, AA, AB, BA, and BB), triads (*e.g.*, AAA, AAB, *etc.*), and so on. For example, the probability of finding AB (or BA) diads is %(AB)=%(BA)=$\overline{R}/2$. If binary copolymers are expressed in terms of the composition m and the run number $\overline{R}$, one obtains a triangular diagram such as shown in Figure 1. We define a completely random copolymer as one in which the probability of finding any diad is given as a product of the compositions of respective components: Then the run number of the completely

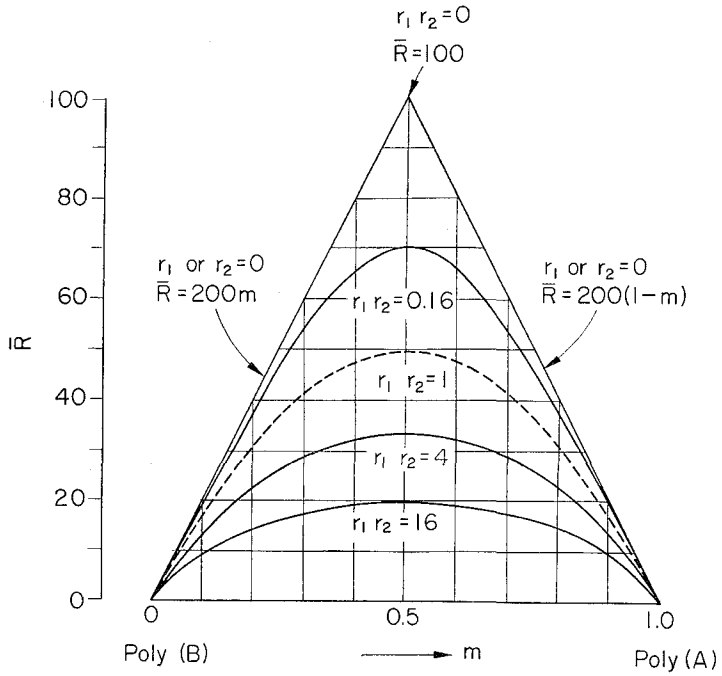

Fig. 1. Triangular diagram for the correlation among composition m, run number $\overline{R}$, and monomer reactivity ratios r_1r_2: dashed curve= completely random copolymer for which $r_1r_2=1$.

random copolymer $\overline{R}_0$ is expressed as:

$$\overline{R}_0 = 200\,m(1-m) \tag{9}$$

(*cf.* Figure 1). The copolymers with $\overline{R}>\overline{R}_0$ may be regarded as having alternating tendency, while those with $\overline{R}<\overline{R}_0$ as having block tendency. Obviously the run number is more appropriately employed for describing so-called random and alternate copolymers. For example, a block copolymer of poly(A)-poly(B) type has $\overline{R}=100\times2/$(degree of polymerization), and that of poly(B)-poly(A)-poly(B) type has $\overline{R}=100\times3/$(degree of polymerization). The run number is less satisfactory for distinguishing such block copolymers. At the moment no direct physical method for determining $\overline{R}$ has been invented. It may be estimated from the knowledge of monomer reactivity ratios for an appropriate copolymerization scheme[8]. For example, on the basis of the so-called terminal model which involves only two reactivity ratios r_1 and r_2, one obtains the relation:

$$\overline{R} = 400\,m(1-m)/[1+\{1+4m(1-m)(r_1r_2-1)\}^{1/2}] \tag{10}$$

from the Lewis-Mayo equation[9] and the Harwood-Ritchey equation[7]. The run number $\overline{R}$ is expressed only by m and r_1r_2: Obviously; if $r_1r_2=1$, $\overline{R}=\overline{R}_0$, *i.e.*, one obtains a completely random copolymer; if $r_1r_2<1$, $\overline{R}>\overline{R}_0$; and if $r_1r_2>1$, $\overline{R}<\overline{R}_0$; if $r_1=r_2=0$, $m=0.5$ and $\overline{R}=100$, *i.e.*, one always obtains a completely alternate copolymer regardless of the composition in monomer feed (*cf.*, Figure 1).

PREPARATION OF STYRENE-METHYL METHACRILATE COPOLYMESRS WITH DIFFERENT ARCHITECTURES

Preparation from a given monomer pair of different types of model copolymers,

each of which has precisely known architecture, is a rather difficult task. Particularly in any convertional process for the synthesis of copolymers the mode of monomer arrangement is controlled automatically by the reactivities of monomers. The reactivities are generally less sensitive to the change of environmental conditions such as temperature, pressure, type of solvents employed, *etc.*[8] Therefore, to prepare copolymers with different modes of monomer arrangement one has to resort to entirely different techniques for the synthesis. For a given pair of monomers, usually techniques available are rather restricted. Recent development, however, has opened up a way for the preparation of model copolymers for certain monomers pairs. Now it is possible to prepare several different types of copolymers from a monomer pair, styrene (ST) and methyl methacrylate (MMA): the anionic polymerization technique[10,8] yields two block copolymers, (PST-PMMA) type and (PMMA-PST-PMMA) type, and a graft copolymer with PST branches on PMMA backbone: the conventional radical polymerization technique[8,9] yields so-called random copolymers which are characterized by the Lewis-Mayo reactivity ratios: the novel cationic polymerization technique developed by Hirooka[11] allows one to prepare alternate copolymers of (—ST-MMA-ST-MMA—) type. A variety can be enhanced through the use of polymer modification techniques, *e.g.*, a radical copolymerization of styrene-methacrylic acid copolymers followed by esterification by diazomethane[12]. The availability of such model copolymers should help to obtain a systematic knowledge on the relation between molecular architectures and properties of copolymers. Below we will describe briefly the processes for the preparation of model copolymers.

Alternate and Statistical Copolymers of Styrene and Methyl Methacrylate: The ST-MMA alternate copolymers are prepared by the method of Hirooka[11]. In the reaction, equimolar complex of MMA monomer and ethyl alminum chloride is prepared first; then ST monomer is mixed with the complex; and the mixture reacts spontaneously (at a temperature anywhere between −78° and room temperature), yielding high molecular weight product. The reaction procedure and the product have remarkable characteristics: (i) neither the complex nor ST monomer alone does not yield polymers under the condition that the copolymerization proceeds sponteneously upon mixing these two species, *i.e.*, $r_1=r_2=0$: (ii) the ST-MMA mole ratio in product is always one to one regardless of the mole ratio in monomer feed: (iii) nmr spectra of the product show no indication of the presence of either ST or MMA triads. All these and othher evidences available so far point to a conclusion that the product should have definitely alternate sequence —ST-MMA-ST-MMA—. Thus the product may be specified as one having $m=0.5$, $\overline{R}=100$.

The ST-MMA random copolymers are usually prepared by radical polymerization method. The choice of conditions (*e.g.*, of initiator, solvent, temperature, *etc.*) is versatile, but such a choice hardly affects the reactivity ratios. The best reported values of the reactivity ratios are $r_1=0.52$ and $r_2=0.46$. (We denote ST and MMA as species A and B, respectively.)[9,8] Using these values, one can predict average composition and its heterogeneity of product from the composition in monomer feed. To obtain a sample with narrow composition heterogeneity, the conversion from monomer to polymer should be suppressed as low as possible,

unless the reaction be carried out at the azeotropic condition[8]. The azeotropic condition is, however, not always available but only for such monomer pairs that have $r_1>1$, $r_2>1$ or $r_1<1$, $r_2<1$. The azeotropic composition is given as $m=(r_2-1)/[(r_1-1)+(r_2-1)]$. From the reactivity ratios one can also estimate the run number $\overline{R}$ as a function of composition m by use of Eq. (10).

Block Copolymers by Anionic Polymerization Method: An ordinary course for the synthesis of block copolymers by anionic polymerization method consists of the following steps. First so-called living poly(A) is prepared by use of an appropriate initiator, *e.g.*, alkyl lithium, solium biphenyl, *etc.* The living poly(A) is either monofunctional (active at only one end) or bifunctional (active at both ends) depending on the type of the initiator. Then second monomer (B) is added to the solution of living poly(A), yielding block copolymers of either poly(A)-poly(B) type or poly(B)-poly(A)-poly(B) type. Anyway, the possible type of block copolymers is detrmined solely by the reactivities of initiators and monomers involved. For example, equally electrophilic monomers such as styrene derivatives (*e.g.*, styrene, α-methyl styrene) and conjugated dienes (*e.g.*, butadiene, isoprene, *etc.*) yield multiblock copolymers of any order and sequences[8]. Whereas less electrophilic polystyryl anion can initiate the polymerization of more electrophilic monomer MMA, but the opposite is impossible, *i.e.*, poly(methyl methacrylate) carbonion does not initiate the polymerization of ST[8,10].

Polystyryl anion can reacts with the ester group of MMA, thus yielding a graft copolymer with PST-branches on a PMMA backbone. In case of the preparation of a linear block copolymer being desired, the occurance of such grafting reaction should be hazardous. Freyss *et al.*[13] has shown that the grafting may be circumvented by adding a few drops of 1, 1-diphenylethylene (DPE) into the solution of living PST, thus styryl carbanions being replaced by less reactive diphenylmethyl carbanions. In Table 1 the molecular weights M_n of block copolymers are compared with those of precursor PST. When DPE is used in the preparation, the molecular weight of PST part of each sample, calculated as $M_n^A=xM_n$ is in agreement with M_n of the precursor: the product copolymer should consist of linear chains.

THERMODYNAMIC AND CONFORMATIONAL PROPERTIES OF COPOLYMERS IN DILUTE SOLUTION

For the analysis of the dilute solution properties of homopolymers[14~16], we have an established concept of the two parameter theories, which describes the thermodynamic and conformational properties essentially by two independent parameters. The parameters are related to the unperturbed dimensions[17] and to the excluded volume effects[14] in a given environment. The unperturbed state, often referred to as the Flory Θ state, may be realized for a given polymer by an appropriate choice of solvent and temperature. The unperturbed dimensions, *e.g.*, the unperturbed mean square statistical radius $\langle S^2\rangle_0$, are directly measurable if the Θ state is realized for a given system to be studied. The excluded volume effect describes the deviation of the dilute solution properties from those of the Θ state due to polymer-solvent (thermodynamic) interactions. Recent advances in the excluded

volume theories[16] have shown that the unperturbed dimensions and the influences of the excluded volume effect may be separately estimated from good solvent data by utilizing their molecular weight dependences.

In case of extending these concepts and procedures based on the two parameter theories to the analysis of copolymer solutions, one ought to ask whether the extension is allowable in the first place. Recent analyses have shown that such is possible at least for random copolymer systems[18~20]. We will discuss the properties of copolymer solutions on the basis of the two parameter theories.

Theta Condition for Copolymer Solutions: The Θ condition[14] for a homopolymer solution is defined as that at which the excess chemical potential due to polymer-solvent interactions is zero and deviation from ideality vanishes. The free energy change accompanying the process of bringing polymer segments (either of a single chain or of different chains) into contact is zero also. Consequently the Θ temperature for a given polymer-solvent system can be identified as the temperature at which the osmotic second virial coefficient A_2 is zero, and also as the critical miscibility temperature in the limit of infinite molecular weight[14]. The concept that the *intra-* as well as the *inter-*molecular excluded volume interactions vanish at the Θ condition immediately leads to an important conclusion that the polymer chain should behave as a random flight chain. Its average dimensions (the unperturbed dimension) are determined solely by the short-range interactions such as the fixed bond length and angles, the steric hindrances between consecutive monomeric units, *etc.*[17]

In a copolymer solution, the situation must be more complex because the excluded volume interactions exist between chemically different units as well as between the same units[22]. The condition exactly analogous to the Θ condition of a homopolymer solution may hardly be realized for a copolymer solution, since for being so the interactions between like and unlike units must vanish simultaneously. Possibly one can locate the temperature at which A_2 vanishes or the critical miscibility temperature in the limit of infinite molecular weight for a given copolymer-solvent system: the temperatures thus determined may be operationally defined as the Θ temperature for the copolymer-solvent system. Following the principle as discussed above, we have examined the Θ temperatures in relation with the molecular architectures for several ST-MMA copolymers. Two different solvents are employed as Θ solvents: one is cyclohexanol (CHL)[23] which is a common Θ solvent with nearly equal Θ temperatures for both PST and PMMA: the other is 2-ethoxyethanol (2-EE)[18] which is a nonsolvent for PST but a Θ solvent for PMMA. Table 2 shows the values of Θ for CHL solutions of several nearly equimolar ST-MMA copolymers[24,12]. The values of Θ (as identified from A_2 data) as functions of composition for ST-MMA random copolymers[18,20] and for (PMMA-PST-PMMA) block copolymers[18] are shown in Table 3 and also in Figure 2. The values of Θ derived from two different sources are in reasonable agreement with each other. It may be said that overall intermolecular excluded volume interactions vanish at these temperasures.

It is of interest to note that the Θ temperatures of the block copolymers are higher than those of the random copolymers, which are still slightly higher than that of the alternate copolymers[24,12]. Particularly, in cyclohexanol the block co-

Table 2. Summary of Θ Temperatures for Equimolar ST-MMA Copolymers.

Code	ST-mol%	Θ Temperatures (°C)[a]		
		Phase Equilibrium	Osmometry	
PST	100	(85.2)	81.8	(83.5)
PST-PMMA	50	—	—	(81.6)
PMMA-PST-PMMA	50±5	81.6	81.3	—
Random (SMA)	52±2	61.8	61.3	(68.6)
Alternate (AL)	50±1	60.8	—	—
PMMA	0	77.0	79.4	(77.6)

[a] Values in parentheses are literature values.

Table 3. Θ Temperatures and $(\partial A_2/\partial T)_\theta$ for ST-MMA Copolymers.

Code	ST-mol%	$10^{-4}M_n$	θ (°C) and $(10^5(\partial A_2/\partial T)_\theta)$			
			2-Ethoxyethanol		Cyclohexanol	
PMMA 14M	0	7.21	39.0	(0.80)	79.4[a]	(2.5)
Random Copolymers						
SM3-7	28.5	35.4	40.0	(0.46)	68.2	(2.3)
SM5-6	55.2	35.0	58.4	(0.52)	61.3	(1.3)
SM7-3	69.4	34.2	72.8	(0.70)	63.0	(1.3)
Block Copolymers						
20B	35.9	15.7	69.5	(0.67)	80.5	(1.8)
15B	48.6	31.7	81.0	(0.33)	81.3	(1.8)
16B	72.4	39.2	Insoluble		84	(1.8)
11B	84.6	19.3	Insoluble		84	(1.8)
PST 16H	100	20.6	Insoluble		81.8[a]	(1.7)

[a] Reported by Froelich and Benoit[23] as θ=77.6°C for PMMA and 83.5°C for PST.

polymers have Θ almost equal to those of PST and PMMA, as opposed to the random and alternate copolymers which have much lower Θ than either of the two homopolymers.

The molecular weight dependence of intrinsic viscosities $[\eta]$ of these Θ solvent systems together with some good solvent systems are shown in Figures 3 and 4 by using now familiar plots of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ due to Stockmayer and Fixman[25]. For the random copolymer systems we would only mention that the intrinsic viscosity at Θ may be expressed as $[\eta]_\Theta = K_o M_w^{1/2}$ in either of the two Θ solvents, and the good solvent data yield the values of K_o which are in practical agreement with those from $[\eta]_\theta$ data[18~21,12]. We may conclude that the intra- as well as the inter-molecular excluded volume interactions vanish simultaneously at the Θ temperature and the random and alternate copolymers behave just as ordinary homopolymers do. On the other hand, for the (PMMA-PST-PMMA) block copolymers, it appears that $[\eta]_\theta$ are proportional to $M_w^{1/2}$ only in CHL but not in 2-EE[18]. The results suggest that the behavior of block copolymers are rather sensitive to the type of solvents: They would not necessarily behave as random flight chains even at the condition of vanishing intermolecular excluded volume interactions (particularly in such a peculiar Θ solvent as 2-EE).

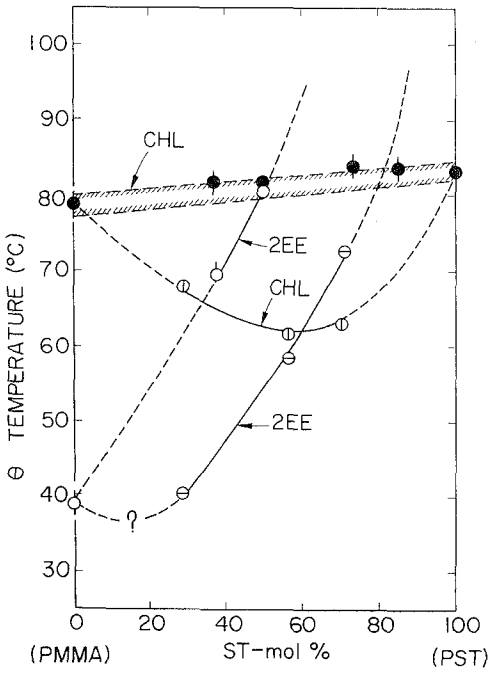

Fig. 2. Values of Θ as a function of composition (in ST-mol%)[18]. (●)= homopolymers and block copolymers in cyclohexanol (CHL); (○)= homopolymer and block copolymers in 2-ethoxyethanol (2-EE); (◑)= random copolymers in CHL; and (⊖)=random copolymers in 2-EE.

The composition dependence of Θ for CHL solutions of the random and the block copolymers[18,23] is rather puzzling. The lower values of Θ for the random copolymers would be interpreted as a result of incompatible (repulsive) interactions between ST and MMA units[18,20,23]. If so, then we don't see why such interactions should not lower the Θ temperatures of block copolymers. On the other hand, a preliminary test has shown that the compatibility of PST and PMMA is fairly good in CHL rather than in other solvents such as toluene[25]. The fact would explain the behavior of the block copolymers but apparently not of the random copolymers. These results suggest a necessity for a reconsideration of the concept of "segments" in copolymer chains. In case of homopolymer chains the theoretical results do not depend on a specific way how a polymer chain is divided into segments; in other words a segment may be arbitrarily defined. On the other hand, for copolymer chains the definition of a segment appears to be a crucial problem: obviously a monomer unit need not be a segment. Murakami[12] has suggested that a sequence longer than diad, at least, should be considered as a segment. These consideration lead to a thought that the alternate copolymer may be regarded as a kind of homopolymer, and then the random copolymer as a ternary copolymer of two homopolymers and the alternate copolymer. This means that the interactions between unlike monomers in random copolymer chains are quite different in nature from those in block copolymer chains.

Unperturbed Dimensions: From the results shown in the foregoing section, it may be said that the unperturbed dimensions may be estimated from the values of K_θ

by use of a relation[14,16]:

$$[\eta]_\Theta = K_o M_w^{1/2};\ K_o = 6^{3/2}\Phi_0\ (\langle S^2\rangle_0/M)^{3/2} \tag{11}$$

Here $\Phi_0(=2.68\times10^{21}$ cgs) is the viscosity constant at the Θ condition[14,26]. Figure 5 shows values of $A^2=(\langle S^2\rangle_0/M_w)$ versus the composition for the ST-MMA random copolymers. Previously Stockmayer *et al.*[1] proposed a simple relation for the values of $\langle S^2\rangle_0/M_w$ of a binary copolymer as:

$$\langle S^2\rangle_0/M_w = x(\langle S^2\rangle_0/M_w)_1+(1-x)(\langle S^2\rangle_0/M_w)_2 \tag{12}$$

where the subscripts 1, and 2 denote the quantities characteristic of the parent homopolymers. In this paticular case of the ST-MMA random copolymers, they appear to be slightly larger than those expected from Eq. (12), implying the presence of extra short range interactions. Recently Matsuda *et al.*[21] reported that the unperturbed dimensions of styrene-methyl acrylate (MA) random copolymers

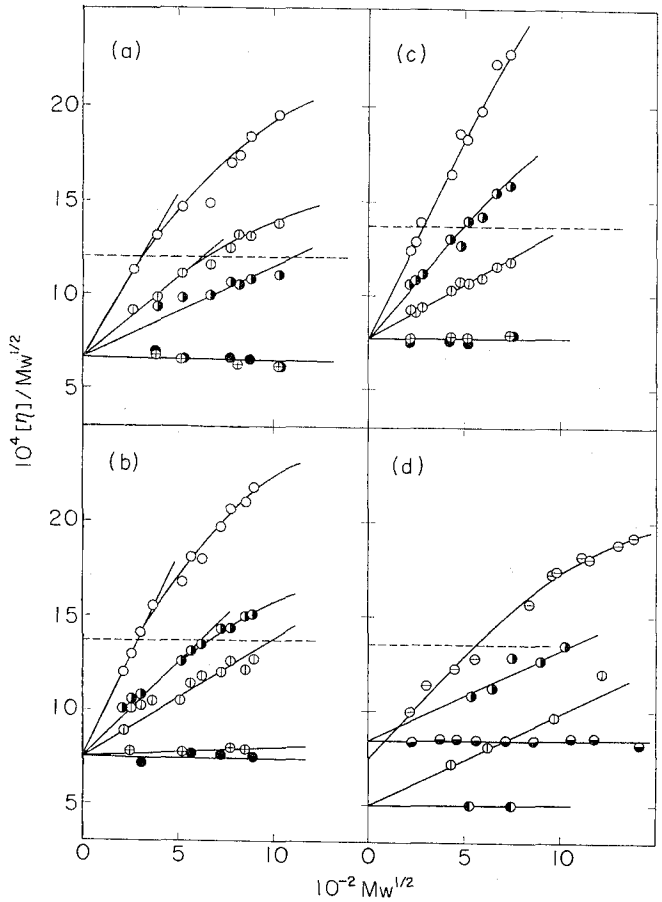

Fig. 3. Plots of $[\eta]/M_w^{1/2}$ *versus* $M_w^{1/2}$ for ST-MMA random copolymers in various solvents[20], (a) SM3 ($m=0.29$); (b) SM5 ($m=0.56$); (c) SM7 ($m=0.70$); Solvents are identified as: (○)=toluene (TOL); (◫)=diethyl malonate (DEM), (◑)=*n*-butyl chloride (1-BC), all at 30.0°; (●)=cyclohexanol (CHL), (⊕)=2-ethoxyethanol (2-EE), at respective Θ. (d) (⊖)=SMA ($m=0.54$)-butanone (MEK) 25°;[1] (◑)=PST-1-BC, 40.8°;[35] (◒)=PST-cyclohexane, 34.5°;[36] (◫)=PMMA-DEM, 30.0°; (◐)=PMMA-1-BC, 40.8°;[35]

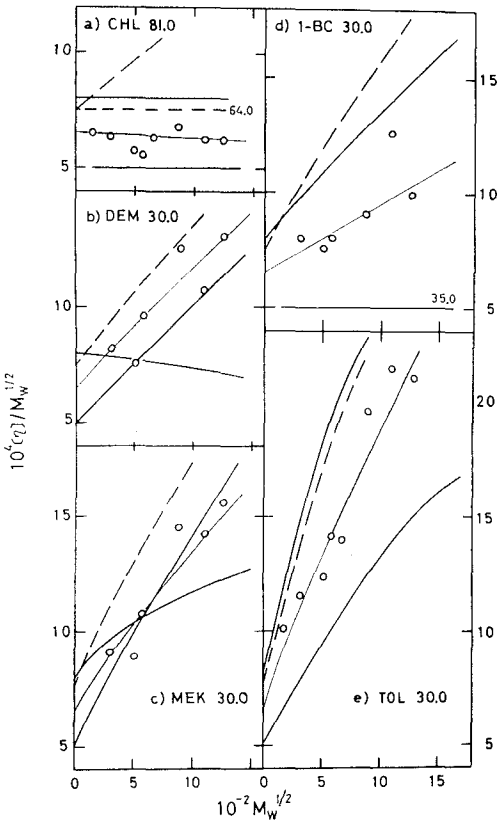

Fig. 4. Plots of $[\eta]/M_w^{1/2}$ *versus* $M_w^{1/2}$ for nearly equimolar ST-MMA copolymers and homopolymers in various solvents at temperatures as indicated. Solvents are identified as in Figure 3. Circles=block copolymers of (PMMA-PST-PMMA) type ; dashed curves=random copolymers SMA (m=0.54); solid curves=PST and PMMA.

may be well approximated by Eq. (12). The unperturbed dimensions of copolymer chains should be a function of the composition, the sequence length distribution (*i.e.*, the population of the linkages between unlike units), the local stereochemical configuration, the bulkiness of side groups, *etc.* In this connection the nmr analysis due to Ito and Yamashita[27] suggests that the local stereochemical configurations of ST-MMA random copolymers are rather atactic, while those of ST-MA copolymers are more nearly isotactic. These facts presumably reflect on the difference of the composition dependence of the unperturbed dimensions between the two systems.

Furthermore, it is of interest to note that the values of K_θ for the nearly equimolar block copolymers observed in CHL are about 15% smaller than those of the corresponding random copolymers[18,24]. Then, the unperturbed dimensions estimated by using Eq. (11) are better approximated by the simple additivity rule, Eq. (12). Each part in the ST-MMA block copolymer chains appears to assume a random flight conformation in CHL at Θ which happens to be quite close to the Θ of both PST and PMMA. The effect of extra-short range interactions between ST-MMA linkages is negligible, because the population of such linkage itself is

negligible in the block copolymer chain. Moreover, the effect of the incompatible interactions between PST and PMMA branches also appears to be absent. The last statement should be valid with some reservations: An observation that the compatibility of PST and PMMA is rather good in CHL than in toluene is favorable for this statement: Whereas the theoretical analysis due to Froelich[28] suggests that a completely segregated chain model for a poly(A)-poly(B) block chain would have $\langle S^2\rangle_0$ larger by a factor of only 15% than that of a corresponding random flight chain, then we might wonder whether the viscometric analysis is sensitive enough to detect this rather trivial change in $\langle S^2\rangle_0$ due to the intra-chain phase separation.

Intrinsic Viscosities in Good Solvents: According to the two parameter theories the excluded volume effects within a single polymer chain are conveniently expressed in terms of expansion factors such as those for mean square molecular radius and for hydrodynamic radius, which are respectively defined as:

$$\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_0\,;\ \alpha_\eta^3 = [\eta]/[\eta]_\theta \tag{13}$$

Then, the expansion factors are expressed as universal functions of an excluded volume parameter z defined as:

$$z = (\langle S^2\rangle_0/M)^{-3/2}BM^{1/2} \tag{14}$$

Here B is the excluded volume parameter related to the binary cluster integral between segments. The parameter B vanishes at $T=\Theta$, and is larger in better solvent. Thus the conformation and other properties of dilute polymer solutions may be described in terms of the two parameters, $\langle S^2\rangle_0$ and z (or $\langle S^2\rangle_0/M$ and B). In fact, one of the central problems in the dilute polymer solution theories is to establish an appropriate procedure for estimating the two parameters separately from adequate data such as $\langle S^2\rangle$ *versus* M or $[\eta]$ *versus* M relations for good solvent systems.

A more agreeable (theoretically) source for the analysis of the excluded volume effects is obtained from $\langle S^2\rangle$ *versus* M relation. However, quantitative measurements of $\langle S^2\rangle$, which are made by light scattering technique[29], are rather difficult even for homopolymer solutions. For copolymer solution, the situation is more complex, because they are affected by the composition heterogeneity[30] in the similar way as in the M_w measurements[1,2], and also because even for a homogeneous copolymer what one observes is not the mean statistical radius but an (apparent) optical radius, *i.e.*, over-all intensities of scattered light from scattering centers (monomers) with different scattering powers[31]. On the other hand, the viscometric method, which is essentially based on the Flory-Fox viscosity equation[14], are applicable to copolymer solutions without much difficulties, although the theoretical basis is less rigid and the method is rather indirect. Nevertheless, viscosity data are certainly an important source to deduce the polymer conformation in solution.

Figures 3 and 4 show plots of $[\eta]/M_w^{1/2}$ versus $M_w^{1/2}$ for the random and block copolymers in several solvents[20,24], each of which has typically different solvent power towards the parent homopolymers. Apparently in all the cases the plots of $[\eta]/M_w^{1/2}$ *versus* $M_w^{1/2}$ for the block copolymers of (PMMA-PST-PMMA) type are between those of the parent homopolymers[24]. Whereas the plots for the

random copolymers are often larger than both of the homopolymers[20]. The block copolymers apparently have smaller values of $[\eta]$ than the corresponding random copolymers as the result that the former have smaller unperturbed dimensions (about 15%), and probably are subjected to lesser influence of the binary interactions between the unlike monomer units. For a quantitative evaluation of these influences, the two parameters, $\langle S^2\rangle_0$ and z, should be estimated for a given system by use of an appropriate theory on the excluded volume effects. However, a satisfactory agreement on the choice of the theories has not yet been reached; hence a quantitative estimate of B (or z) is not possible in a satisfactory manner[32]. Nevertheless, so far as one is concerned with a qualitative comparison, say, between the B values of copolymers with different architectures, any theory would provide an essentially similar conclusion[20,21]. Figure 5 shows the dependence of B on composition for the statistical copolymers[20].

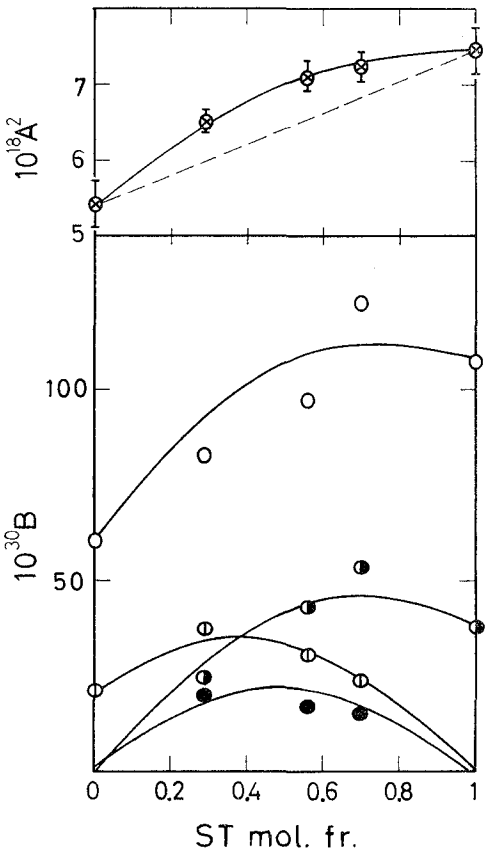

Fig. 5. Values of $A^2=(\langle S^2\rangle_0/M)$ and B as functions of composition for ST-MMA random copolymers. Solvents are identified by the symbols as in Figure 3. Temperatures are 30.0° except for CHL systems in which T=80.0°.

Stockmayer *et al.*[1] suggested that the parameter B for binary copolymer may be written approximately as:

$$B = mB_1=(1-m)B_2+2m(1-m)\Delta B_{12} \tag{15}$$

where the subscripts 1 and 2 again denote the quantities characteristic of the parent homopolymers; ΔB_{12} is an extra-interaction term between unlike monomer units, and is supposed to be independent of solvent but characteristic of the parent homopolymer species[1]. In fact, all the data[20] shown in Figure 5 can be well approximated in the form of Eq. (15), *i.e.*,

$$B = mB_1 + (1-m)B_2 + 2m(1-m)(45 \pm 5) \times 10^{-30} \tag{16}$$

On the other hand, for the (PMMA-PST-PMMA) block copolymers (although only the data for nearly equimolar samples are available a the moment) values of B appear to be expressed as:

$$B = mB_1 + (1-m)B_2 \tag{17}$$

As opposed to the random copolymers, the contribution of interactions between unlike units again seems to be unimportant for the block copolymer systems.

Froelich[23] has treated the excluded volume effect in a copolymer chain on the basis of the method of Fixman[33]. The results for equimolar ($m=0.5$) random copolymers and block copolymers of poly(A)-poly(B) type are, respectively, given as:

$$B = 0.5(B_1 + B_2) + 0.5\Delta B_{12} \text{ (random)} \tag{18a}$$

$$B = 0.5(B_1 + B_2) + 0.306\Delta B_{12} \text{ (block)} \tag{18b}$$

The theory appears to predict the behavior qualitatively, but is still not completely. A reason for the apparent absence of the incompatible interaction term for block copolymer chains is not clear at the moment: This might be due to minimal frequencies in the intersegmental contacts, or else this might be due to vanishingly small value in ΔB_{12} for block copolymers.

As to the conformations of block copolymers in good solvents, the occurrance of "intramolecular phase separation" is often suggested. However, a preliminary study on the phase equilibrium of a ternary system (two polymers-one solvent) shows that the critical miscibility concentration c_m is in general higher for the blend with lower molecular weight, and becomes lower as the molecular weight increases; and the concentration is rather high[34,24]. On the other hand, the effective concentration in the domain of a single polymer coil decreases with increasing molecular weight. In view of these facts, the "intramolecular phase separation" would be realized as a result of rather delicate balance between these opposing effects. Possibly the phenomenon would take place in a solvent in which the homopolymer pair has very poor compatibility. Thus we would propose a "partially segregated chain" model for the conformations of block copolymer chains: The extent of segregation would depend on the compatibility of the homopolymer pair in the particular solvent to be studied.

Finally it should be noted that the discussion given so far has not established fully the identity between the intra- and interchain excluded volume interactions for block copolymer chains. A theoretical analysis[37] suggests that they are not identical. Interestingly our preliminary results show that the dimensionless ratios $A_2M/[\eta]$ for the ST-MMA block copolymer-toluene systems vary between 100-130, which are indistinguishable from the typical values for homopolymers[16] and random copolymers[20]. This is a subject of a further extensive study.

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